# *In -situ*, High Temperature Study of Phase Transformations in Ceramics


## Professor W. M. Kriven

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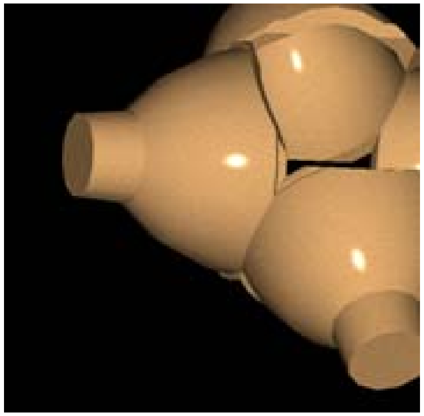
LOWENBRÄU

# Goal of this work

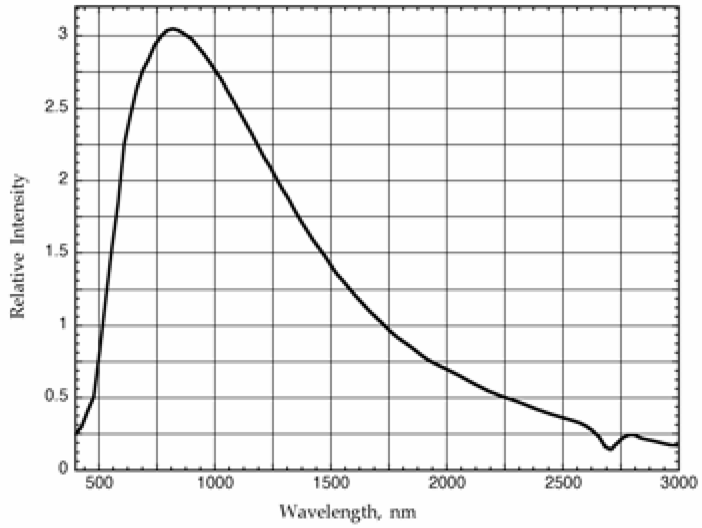
- To explore the feasibility of using the thermal-image technique to study reversible, displacive-type phase transformations, specifically in air, at elevated temperatures

- To measure their lattice parameters as a function of temperature and determine their axial thermal expansion coefficients, transformation temperatures and unit cell volume/shape changes

# Halogen lamp



Osram Xenophot
HLX 64635
15V 150W

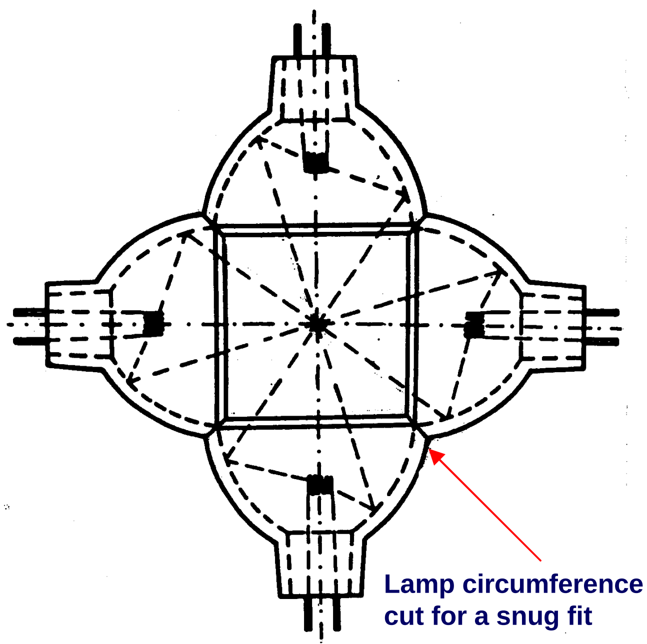



Radiation of the halogen lamp

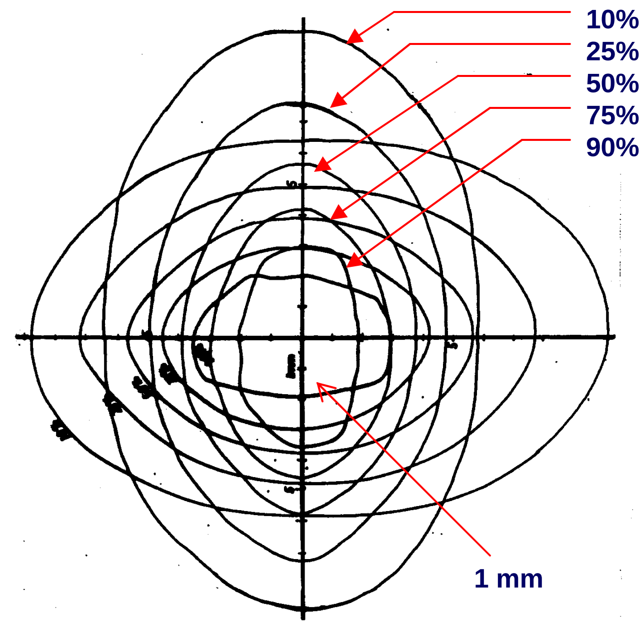
# A Compact Thermal-image Furnace

<u>Heat source</u>: **halogen infrared reflector lamp (OSRAM Xenophot HLX64635)**

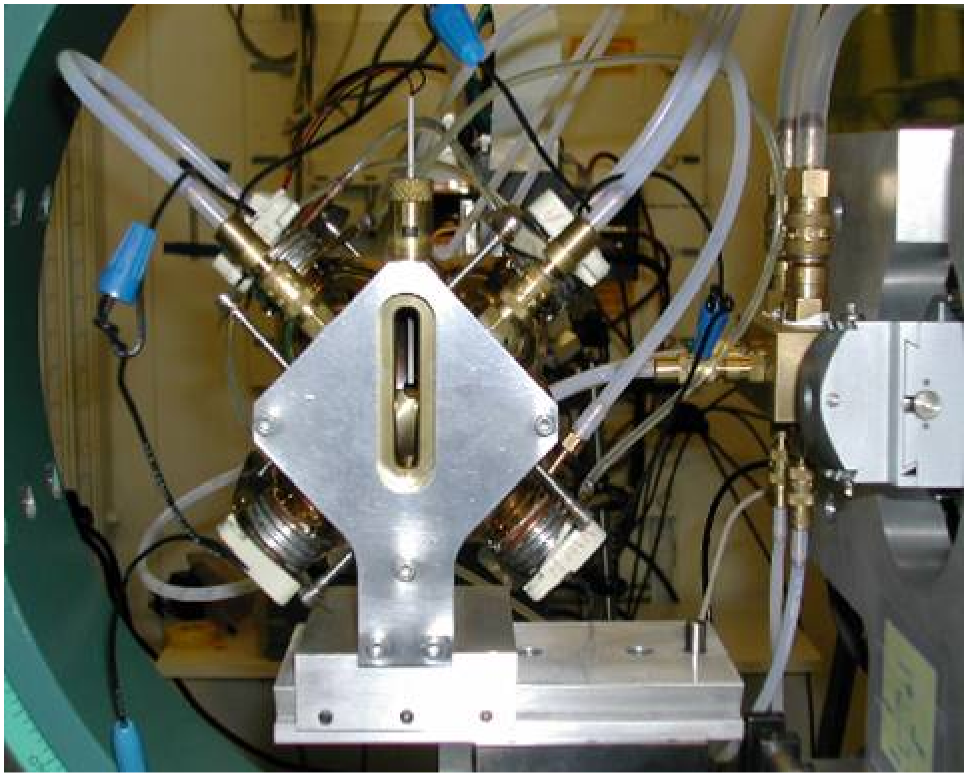
**4 lamps (50mm diameter, 150W) arranged to have a common focus**




**Intersection of filament image → "hot-spot" at the common focus**



# High Temperature Furnace



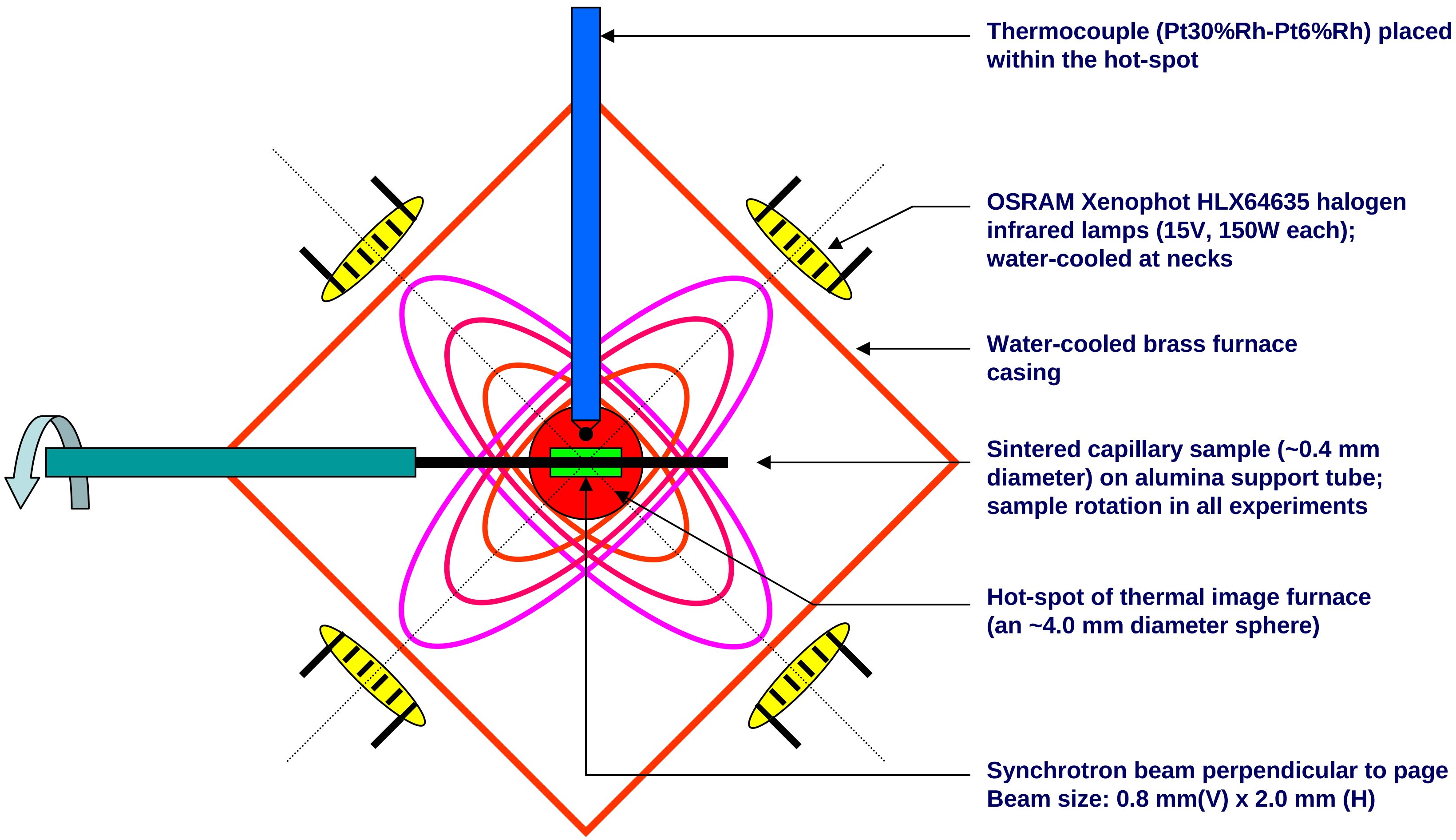
Setup at UNICAT beamline 33BM at APS;
Argonne National Laboratory

Water cooling

Goniometer for
specimen rotation

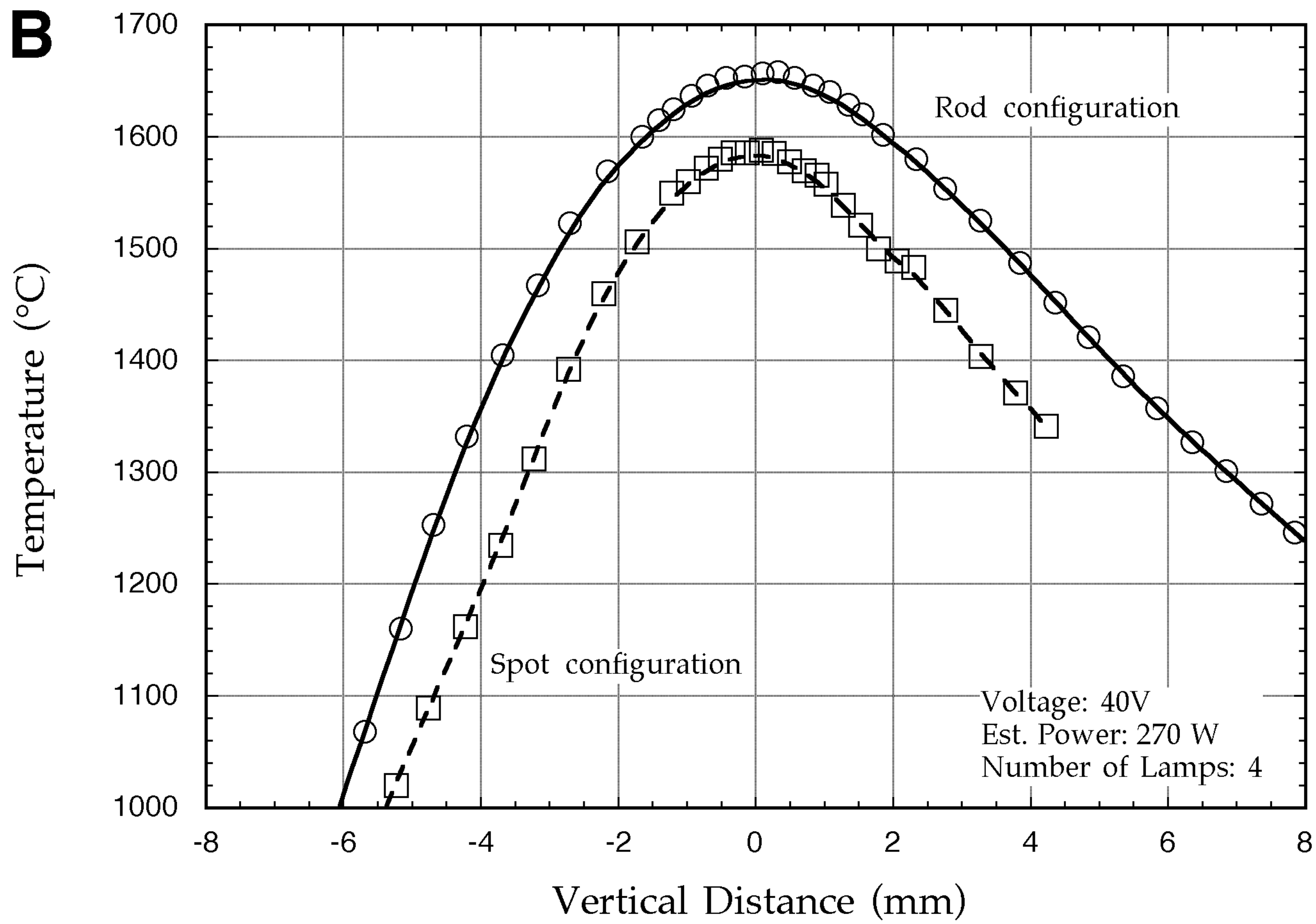
Thermocouple

# Layout

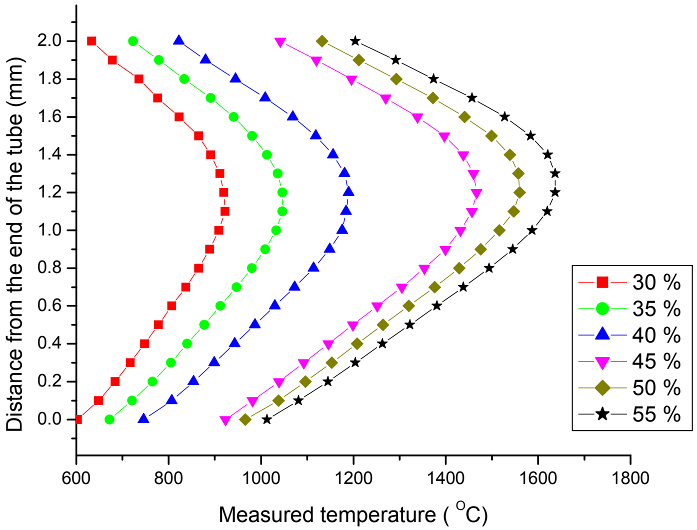


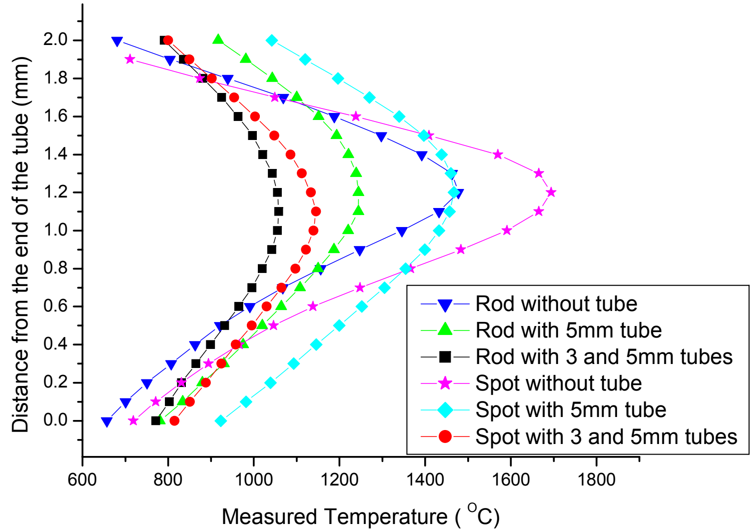
Thermocouple (Pt30%Rh-Pt6%Rh) placed within the hot-spot
OSRAM Xenophot HLX64635 halogen infrared lamps (15V, 150W each); water-cooled at necks
Water-cooled brass furnace casing
Sintered capillary sample (~0.4 mm diameter) on alumina support tube; sample rotation in all experiments
Hot-spot of thermal image furnace (an ~4.0 mm diameter sphere)
Synchrotron beam perpendicular to page
Beam size: 0.8 mm(V) x 2.0 mm (H)

# Temperature Profile of Quadrupole
## (at 2/3 power)



# Temperature measurement

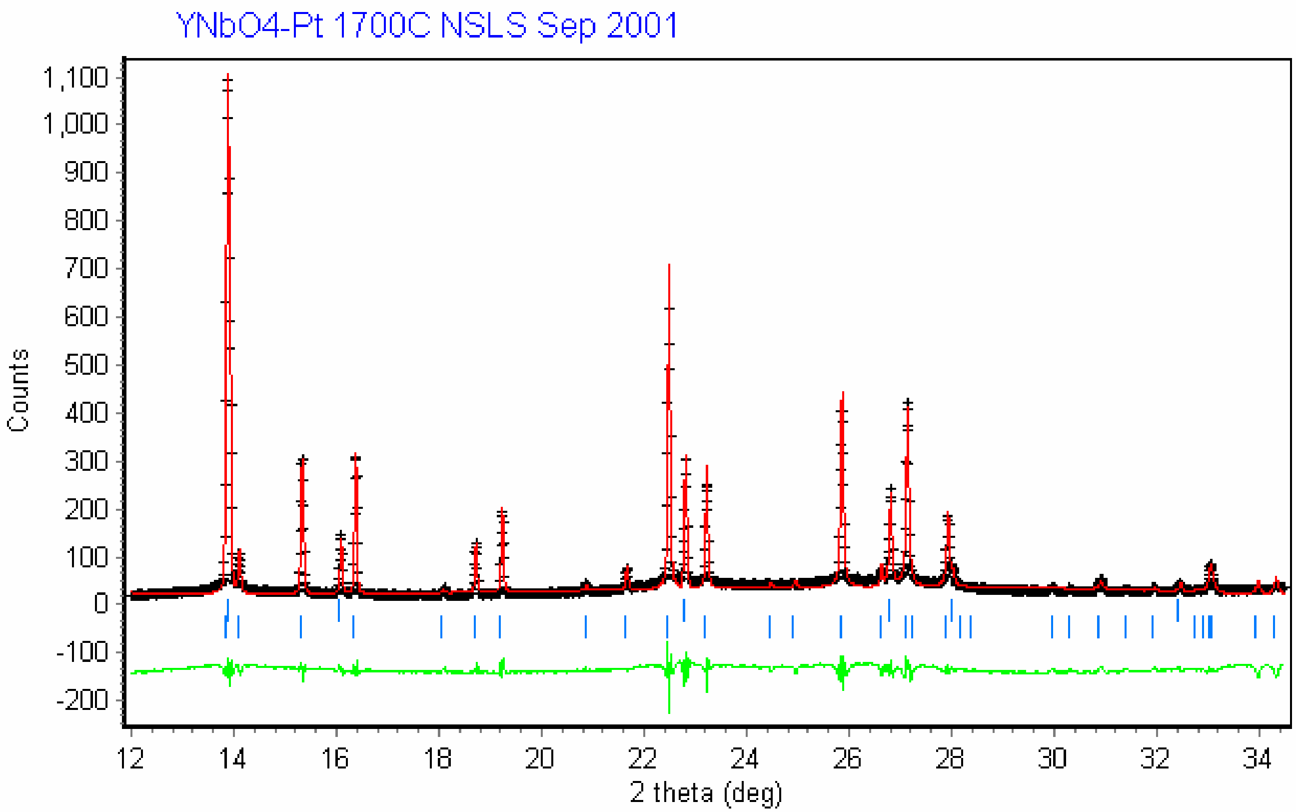



Temperature measurement
Hot spot with $Al_2O_3$ tube
(OD : 5 mm, ID : 4 mm)

Temperature measurement with change of lamp and tubes

# *In-situ* HTPXRD: $RNbO_4$ (R = Dy, Y)

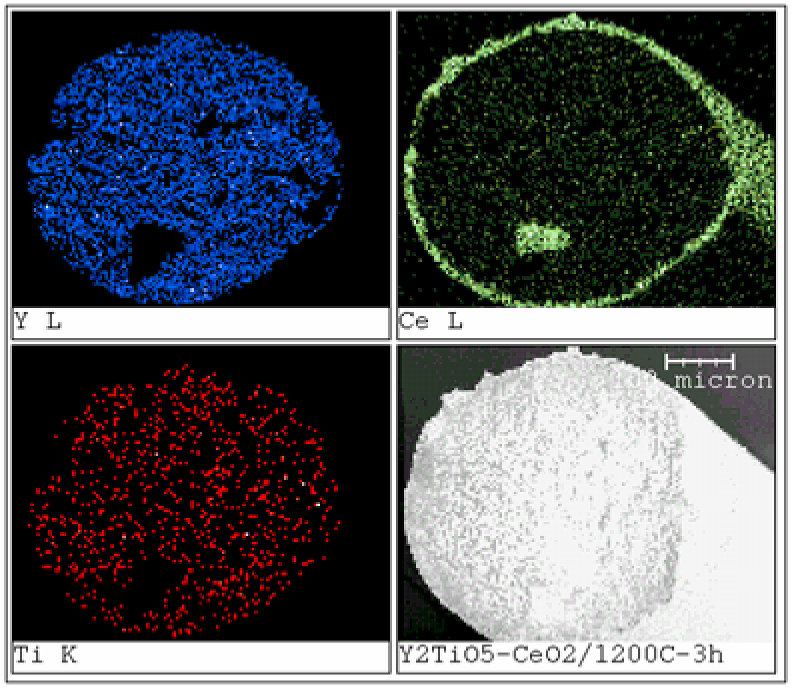



**Obvious TDS indicating attainment of very high temperatures *in-situ* in air in this work**

# Preparation of Capillary Sample

- **Powder preparation**
  - **PVA method**
  - **ethylene glycol method**
- **Capillary fabrication**
  - **extrusion**
  - **"controlled" sintering**
- **"Thermometer" coating**
  - **platinum ink**
  - **oxide layer**

    **($CeO_2$ mp: 2300°C, MgO mp: 2800°C)**




**A representative capillary sample (diameter ~0.35 – 0.40 mm)**

# Temperature Calibration

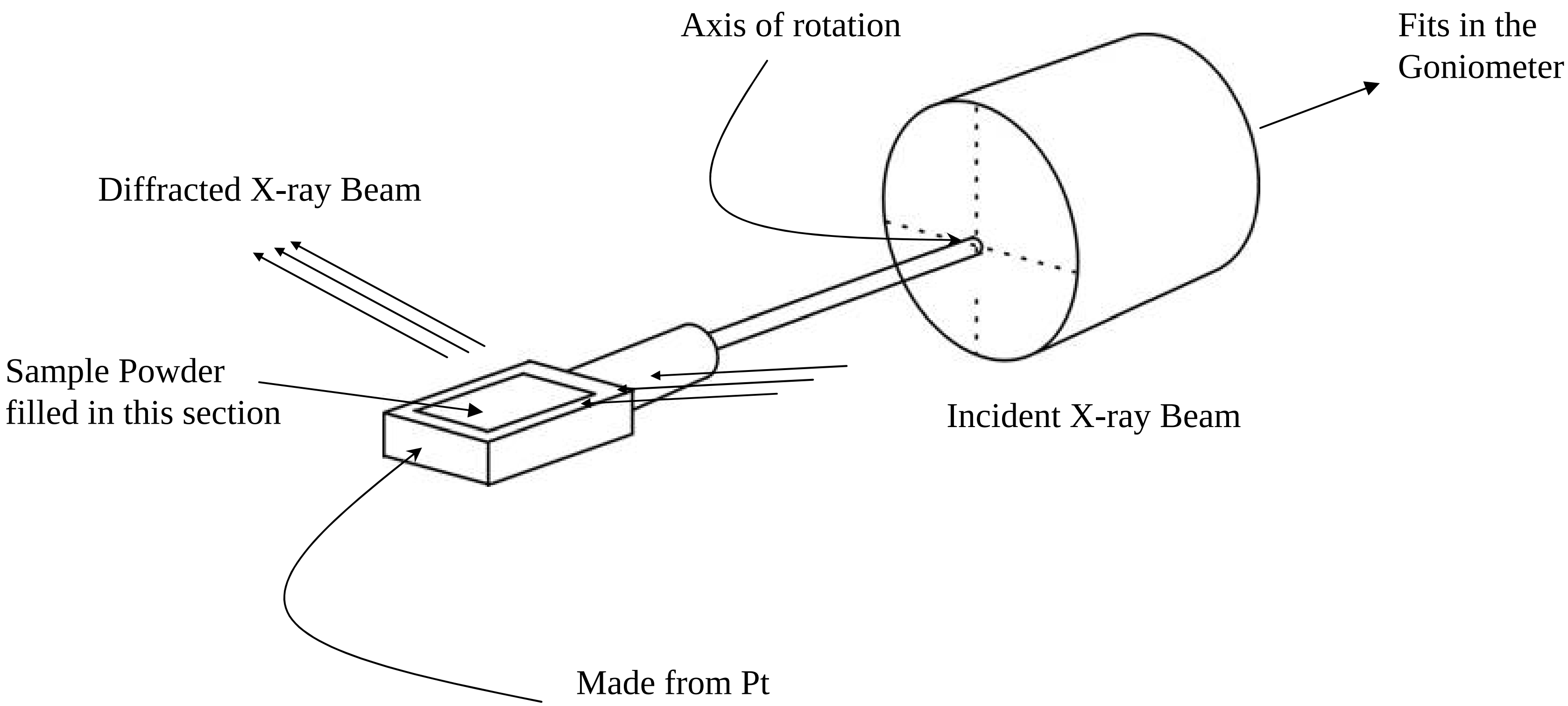
**Up to 1700 °C**

- **Thermocouple Pt 30% Rh - Pt 6% Rh in close proximity to specimen**
- **Accuracy ±10 °C at 1500 °C**

**Above 1700 °C**

- **Lattice constant of coating material**
- **Furnace power calibration with known melting points and phase transformations**
- **Accuracy ±30 °C at 2000 °C**

# Reflection Geometry for *in-situ* high temperature phase transformation studies at UNICAT 33BM Beam line at APS



# Advantages

- In situ studies of lattice parameter development and phase transformations possible up to 2000 °C
- In air studies
- Quick temperature ramping
- 
- Easy sample preparation

# Problems

**Temperature calibration**

- **Insufficient known calibration materials**
- **Thermal expansion mismatch between coating and specimen**
- **Reaction between calibration material and specimen under study**

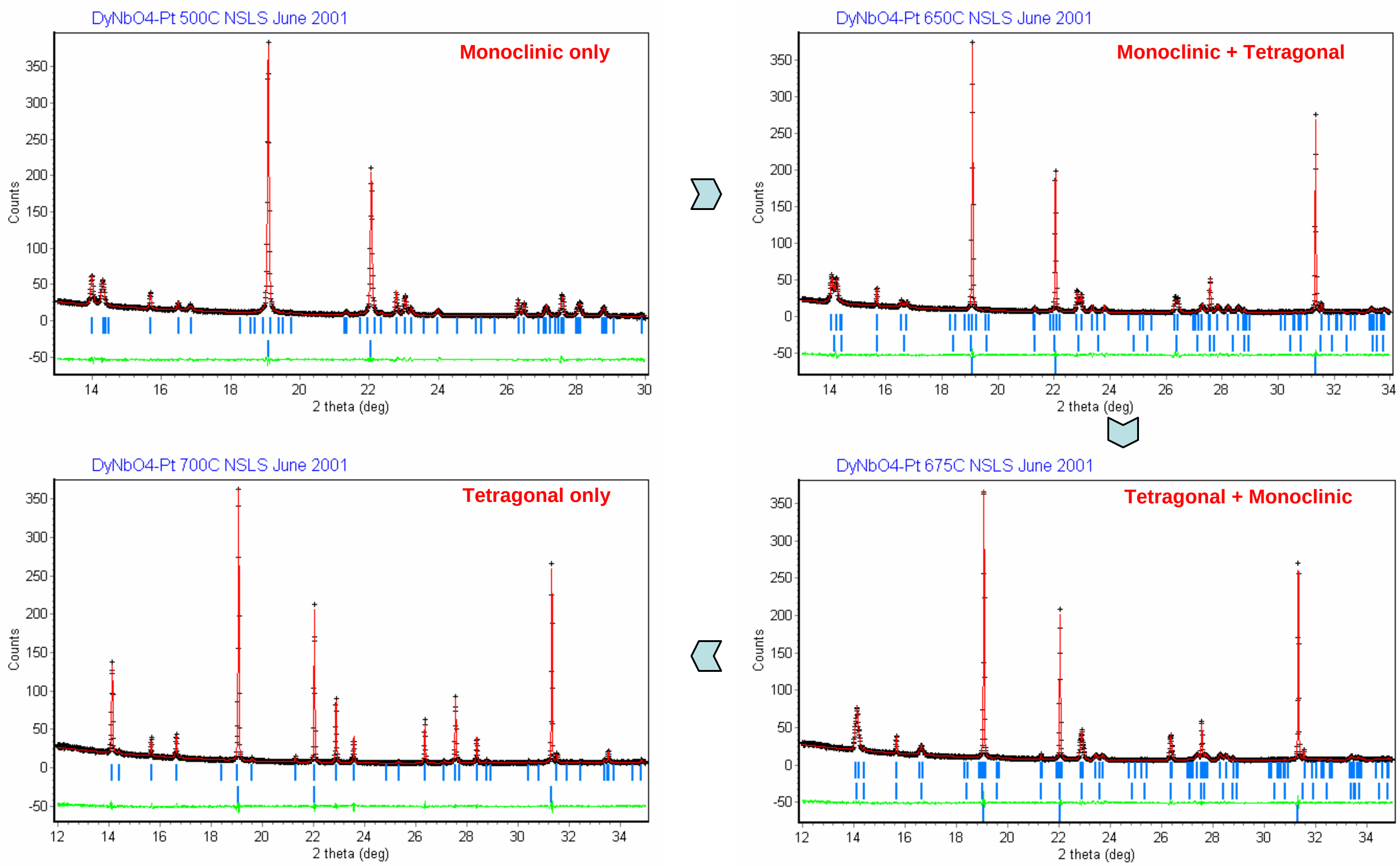
**Specimen stability**

- **Structural (specimen disintegrating, glassy phase)**
- **Chemical stability**

**X-ray absorption by heavy elements in Debye-Scherrer geometry**

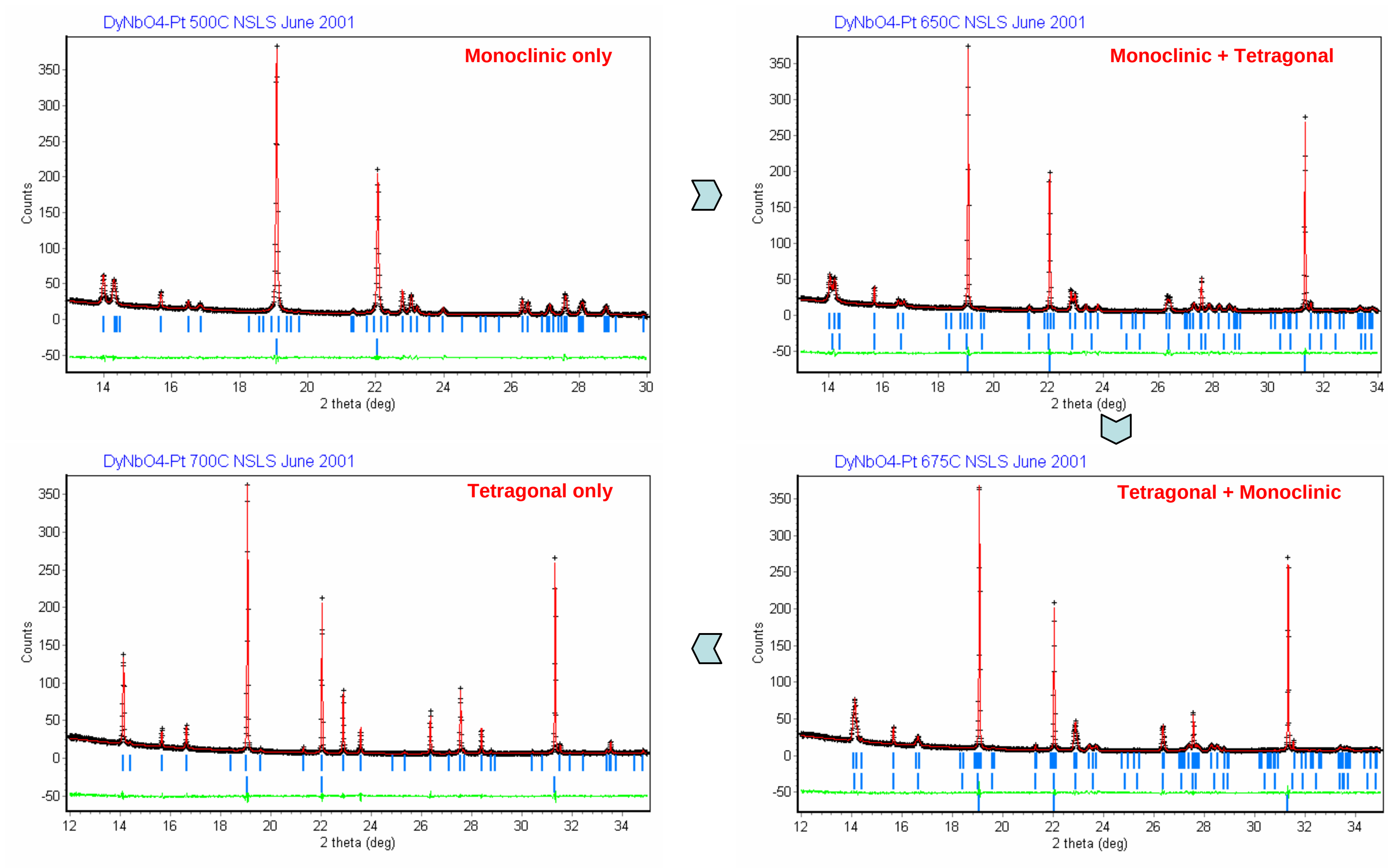
**Thermal expansion of sample holder in Bragg-Brentano geometry**

# *In-situ* HTPXRD in Air: $RNbO_4$ (R = Dy, Y)




**$DyNbO_4$: monoclinic → tetragonal transformation**

# *In-situ* HTPXRD in Air: $RNbO_4$ (R = Dy, Y)




$DyNbO_4$: monoclinic $\rightarrow$ tetragonal transformation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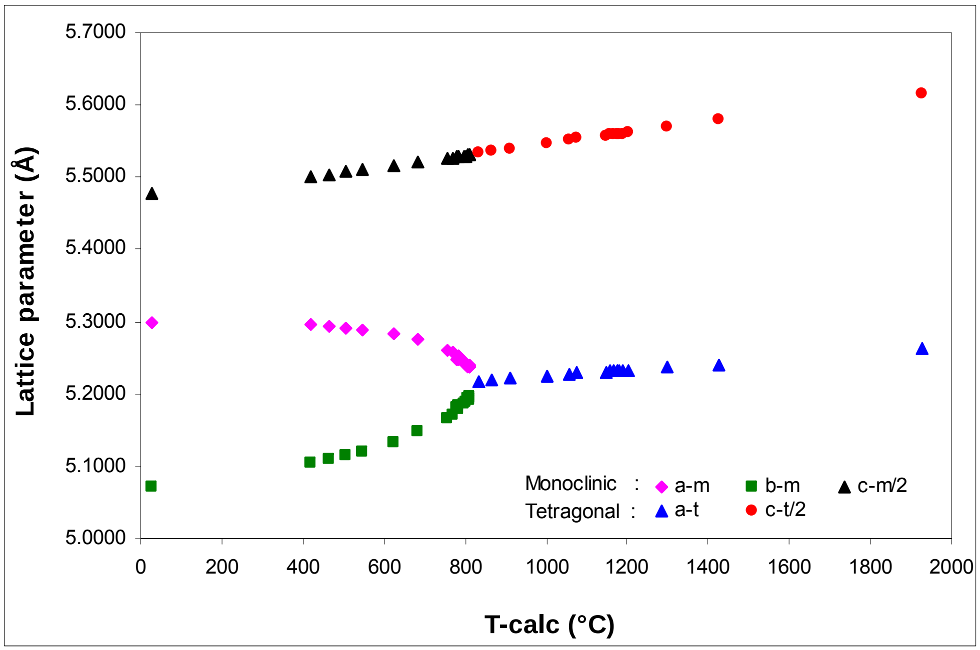
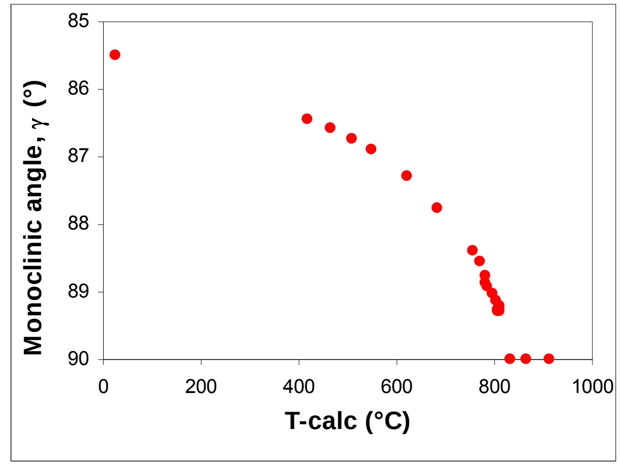
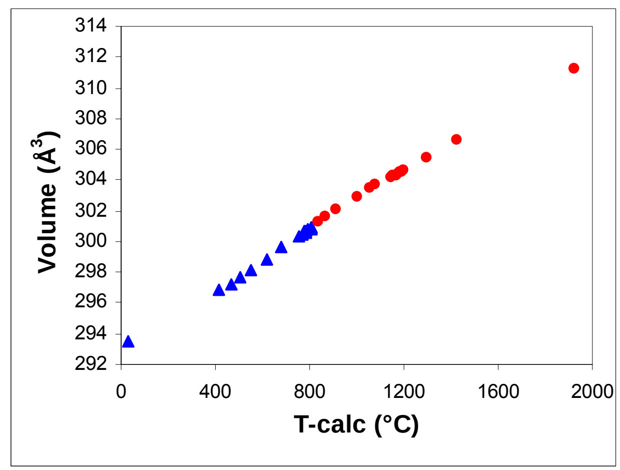
# *In-situ* HTPXRD in Air: $RNbO_4$ (R = Dy, Y)

## $YNbO_4$: monoclinic-to-tetragonal transformation




**Temperature evolution of**
**a, b, c, γ and unit cell volumes**



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# Conclusion for $LnNbO_4$

- the monoclinic-to-tetragonal transformation
  - in $YNbO_4$ is 2nd order at ~830 °C
  - the room temperature spontaneous strain of $YNbO_4$ is 6.35%

| Compound | Crystal Symmetries | Transformation Temperature (To on cooling) | Volume Change ($\Delta V$) | Unit Cell Shape Change(°) |
|---|---|---|---|---|
| $ZrO_2$ | Tetragonal → monoclinic | 950 | (+)4.9% (R.T.) | 9 |
| $Ln_2O_3$ (type) | monoclinic → cubic | 600—2200 | (+)10% | 10 |
| $Ca_2SiO_4$ ($K_2SO_4$-type) | monoclinic → orthorhombic | 490 | (+)12% | 4.6 |
| $Sr_2SiO_4$ ($K_2SO_4$-type) | orthorhombic →monoclinic | 90 | 0.2% | 2 |
| NiS | rhombohedral → hexagonal | 379 | (+)4% | – |
| $2Tb_2O_3.Al_2O_3$ (type) | orthorhombic →monoclinic | 1070 | (+)0.67% | 18.83 |
| $PbTiO_3$ | cubic → tetragonal | 445 | (+)1% | 0 |
| $KNbO_3$ | tetragonal → orthorhombic | 225 | ~0% | 0 |
| $LuBO_3$ | hexagonal → rhombohedral | 1310 | (+)8% | – |
| $MgSiO_3$ ($CaSiO_3$-type) ($FeSiO_3$-type) | orthorhombic →monoclinic | 865 | (-)5.5% | 18.3 |
| $YNbO_4$ ($LnNbO_4$-type) | tetragonal →monoclinic | 900 | (-) 1.8% | 4.53 |
| $LnBO_3$ (type) | hexagonal→ hexagonal | 550—800 | (-)8.2% | – |

**Table 1. Examples of First Order Displacive Transformations in Ceramics**

| Compound | Crystal Symmetries | Transformation Temperature (To on cooling) | Volume Change ($\Delta V$) | Unit Cell Shape Change(°) |
|---|---|---|---|---|
| Cristobalite ($SiO_2$) | cubic → tetragonal | 265 | (-) 2.8% | 0 |
| Hexacelcian ($BaAl_2Si_2O_8$) | hexagonal → orthorhombic | 300 | (-) 0.43% | 0 |
| Leucite ($KAlSi_2O_6$) | cubic → tetragonal | 620 | ~0 | 0 |
| Zircon ($ZrSiO_4$) | monoclinic → tetragonal | 827 | ? | ? |
| Di-lanthanide aluminates ($Ln_4Al_2O_9$) | monoclinic → monoclinic | 1400 | (+) 0.5% | ? |
| Di-lanthanide titantes ($Ln_2TiO_5$) | hexagonal → orthorhombic | 1712 | ? | 0 |
| Barium orthotitanate ($Ba_2TiO_4$) | ? | ? | ? | ? |
| Cerium pyrosilicate ($CeSiO_4$) | ? | ? | ? | ? |
| Aluminum titanate ($Al_2TiO_5$) | ? | ? | ? | ? |
| Lithium phosphate ($Li_2PO_4$) | ? | 340 | ? | ? |
| Lanthanide (eg.Gd) vanadates ($LnVO_4$) | monoclinic → tetragonal | 825 | ? | ? |

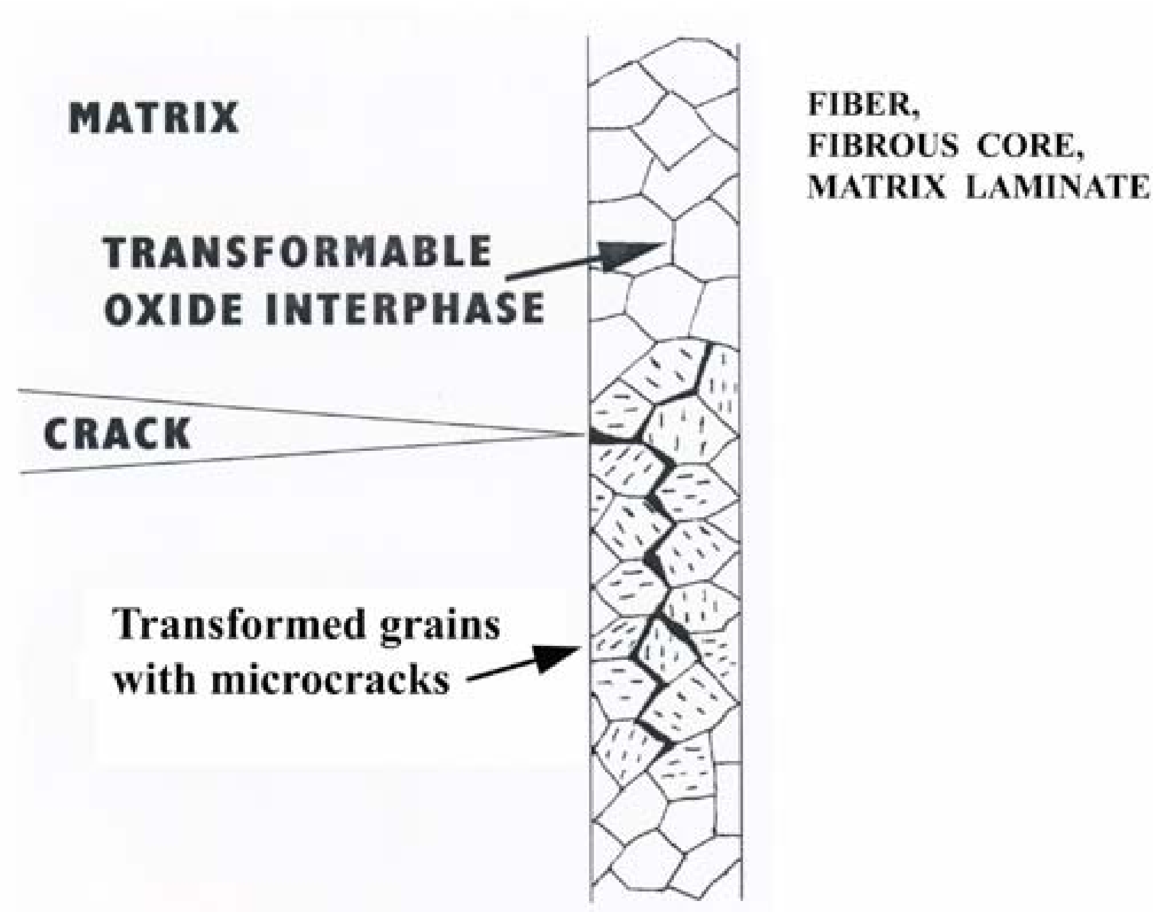
Table 2. Other Examples of Phase Transformations in Ceramics

## Table 3. RARE-EARTH OXIDES : PHASE TRANSFORMATIONS

<table>
<tr><th>Compound</th><th>La</th><th>Ce</th><th>Pr</th><th>Nd</th><th>Pm</th><th>Sm</th><th>Eu</th><th>Gd</th><th>Tb</th><th>Dy</th><th>Ho</th><th>Er</th><th>Tm</th><th>Yb</th></tr>
<tr><td>$LnNbO_4$ scheelite</td><td colspan="14">Monoclinic (low T) → Tetragonal (high T)</td></tr>
<tr><td>$Ln_2TiO_5$</td><td colspan="6">Orthorhombic</td><td colspan="5">Orthorhombic (low T) → Hexagonal → Cubic</td><td colspan="3">Cubic</td></tr>
<tr><td>$LnAlO_3$ Perovskite</td><td colspan="4">Rhombohedral (low T) → Cubic</td><td colspan="2">Rhombohedral (low T) → orthorhombic → Cubic</td><td colspan="2">Rhombohedral (low T) → orthorhombic</td><td colspan="6">Orthorhombic</td></tr>
<tr><td>$LnTaO_4$</td><td colspan="3">Unknown structure</td><td colspan="8">Monoclinic (low T) → Tetragonal</td><td colspan="3">Monoclinic</td></tr>
<tr><td>$LnVO_4$</td><td colspan="2">Monoclinic (?)</td><td colspan="12">Tetragonal $YPO_4$ structure</td></tr>
<tr><td>$LnAsO_4$</td><td colspan="4">Monoclinic $CePO_4$ structure</td><td colspan="10">Tetragonal $YPO_4$ structure<br>Tetragonal scheelite ($CaWO_4$) structure (high pressure)</td></tr>
<tr><td>$LnPO_4$</td><td colspan="8">Monoclinic $CePO_4$ structure</td><td colspan="6">Tetragonal $YPO_4$ structure</td></tr>
<tr><td>$Ln_2Ti_2O_7$</td><td colspan="4">Monoclinic</td><td colspan="10">Cubic (pyrochlore)</td></tr>
<tr><td>$Ln_3NbO_7$</td><td colspan="4">Tetragonal (?)</td><td colspan="3">?</td><td colspan="4">Hexagonal</td><td colspan="3">?</td></tr>
</table>

MSE at Illinois

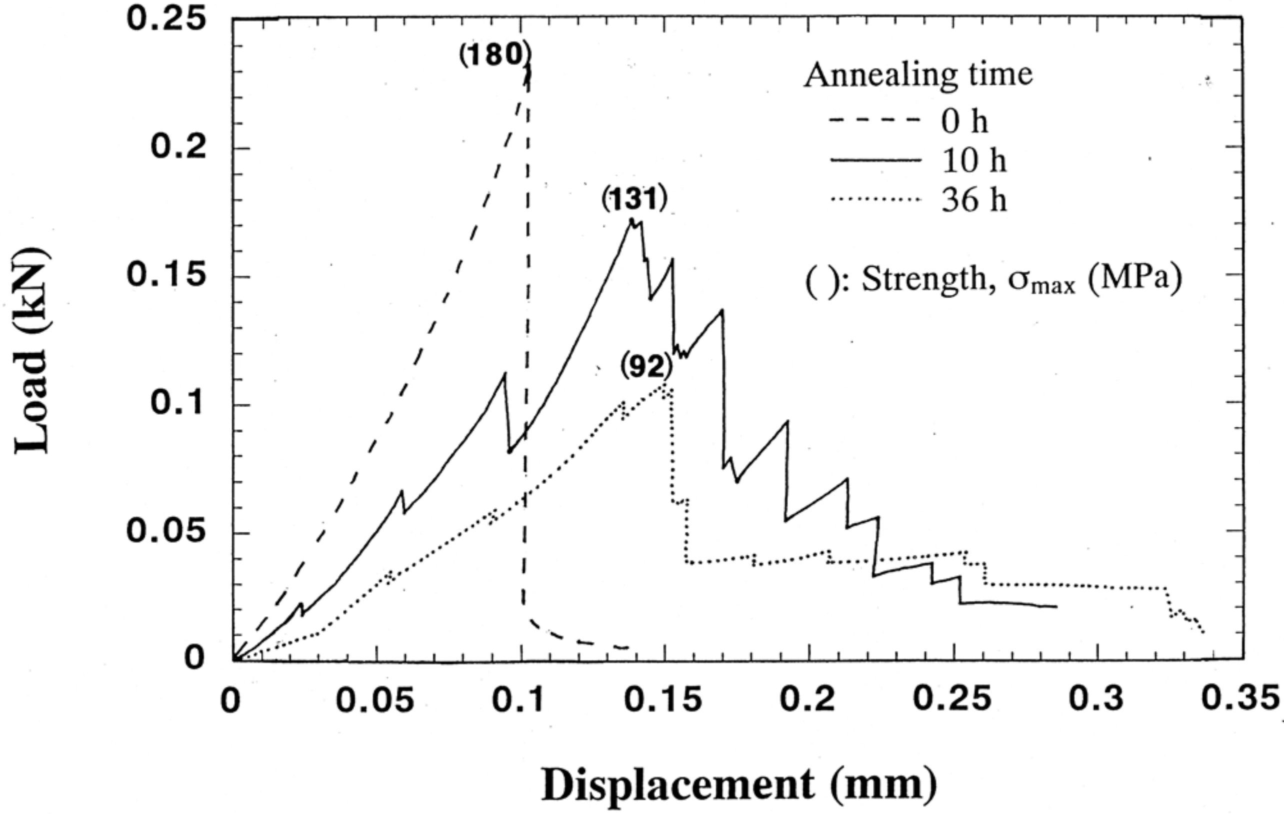
# Toughening of Ceramics by Transformation Weakening of Interphases



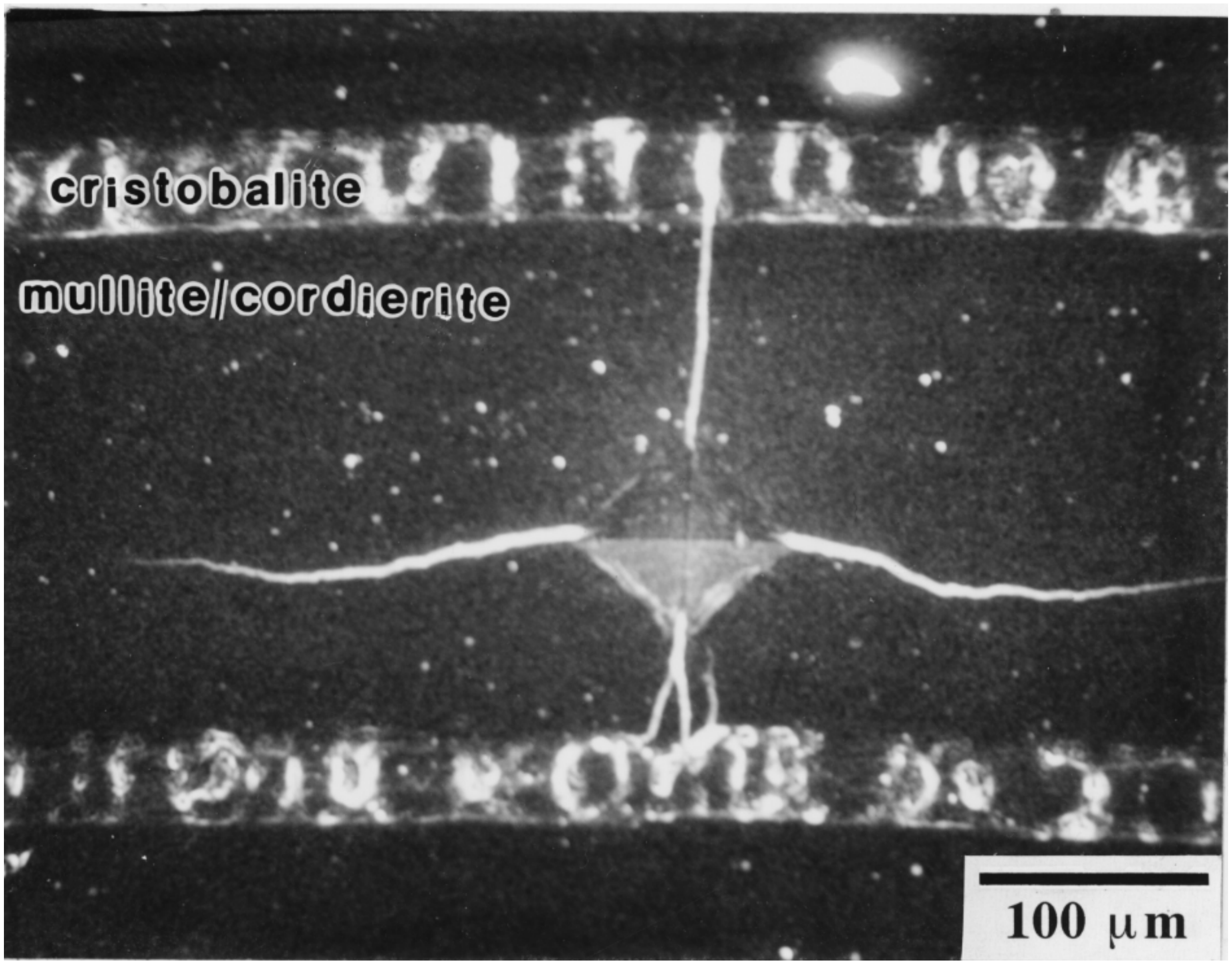
# Toughening Mechanism

- Schematic diagram  illustrates “transformation weakening of ceramic interphases” leading to overall toughening of a ceramic matrix composite.
- In thermally induced transformations, all interphases are pre-transformed before the approach of a crack, with some consequent loss of overall strength of the material.
- In the ideal, shear-stress induced case, an oncoming crack induces a transformation in its immediate environment, with strength only minimally reduced throughout the bulk.
- Maximum toughening is achieved, since the propagating crack needs to do work to overcome the nucleation barrier and cause transformation, and onset of the other synergistic toughening mechanisms (e.g., crack formation) occurs.

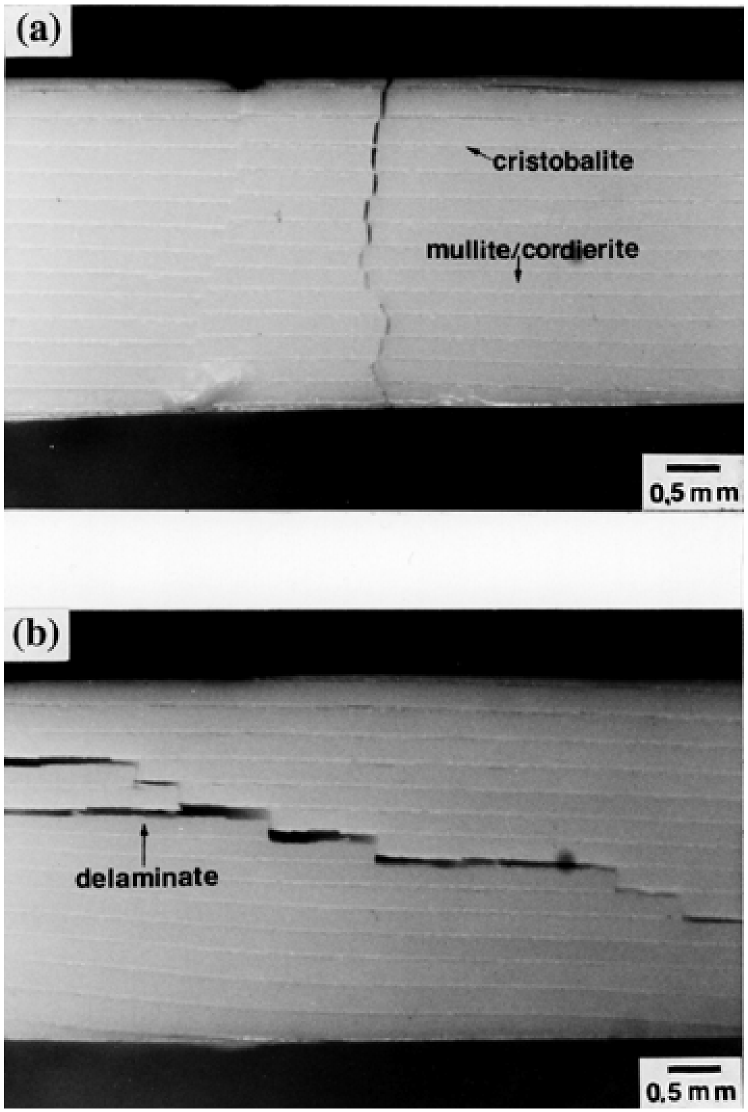
# Work of Fracture of TW Weakened Composite



# Preferential Crack Deflection along TW Interphases



# Toughening by TW of Interphases



## Long term vision for study of phase transformations in structural ceramics and composites

**Displacive phase transformations can be accompanied by volume changes and/or by shape changes**

**Large volume changes ($\Delta V$)**

- **"Transformation toughening" (e.g. zirconia ceramics)**
- **"Transformation weakening" of interphases, giving overall toughening of fiber-reinforced composites or fibrous monoliths (e.g. enstatite, cristobalite)**

**Structural ceramics for airplane and**

**Ground-based turbine engines**

**Unit cell shape changes ($\Delta\beta$)**

- **Ferroelastic phase transformations**
- **Ferroelasticity**
- **Toughening by "twin filipping"**

**Large force actuation**
**(e.g., for MEMS devices)**
**Shape memory ceramics**